

OFFICE OF NAVAL RESEARCH

GRANT : N00014-89-J-3062

R&T Code 3132084

Technical Report No. 45

Low Band Gap Planar Conjugated Pyrrole-Derived Polymers. Optical Absorbances From the UV to the Near-IR

by

T. W. Brockmann and J. M. Tour

Accepted for Publication in

*Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, 35(2), 693.

Department of Chemistry and Biochemistry  
University of South Carolina  
Columbia, SC 29208

June 7, 1995

Reproduction in whole, or in part, is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited.

DTIC QUALITY INSPECTED 5

19950705 056

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 6-7-95		3. REPORT TYPE AND DATES COVERED Technical Report	
4. TITLE AND SUBTITLE Low Band Gap Planar Conjugated Pyrrole-Derived Polymers. Optical Absorbances From the UV to the Near-IR.				5. FUNDING NUMBERS G- N00014-89-J3062 R&T 3132084	
6. AUTHOR(S)  T. W. Brockmann' and J. M. Tour				K. Wynne	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry and Biochemistry University of South Carolina Columbia, SC 29208				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Navy Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000				10. SPONSORING/MONITORING AGENCY REPORT NUMBER  45	
11. SUPPLEMENTARY NOTES  Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 1994, 35(2), 693.					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  Described will be the synthesis of a pyrrole-derived polymer that can exist in a zwitterionic form ( $\lambda$ = 520 nm), a partially reduced form ( $\lambda$ = 290 nm), or a planar form ( $\lambda$ = 900 nm). The absorptions are reversible depending on the pH of the medium.					
14. SUBJECT TERMS				15. NUMBER OF PAGES	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	
				20. LIMITATION OF ABSTRACT UL	

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)  
Prescribed by ANSI Std. Z39-18  
298-102

# Low Band Gap Planar Conjugated Pyrrole-Derived Polymers. Optical Absorbances From the UV to the Near-IR

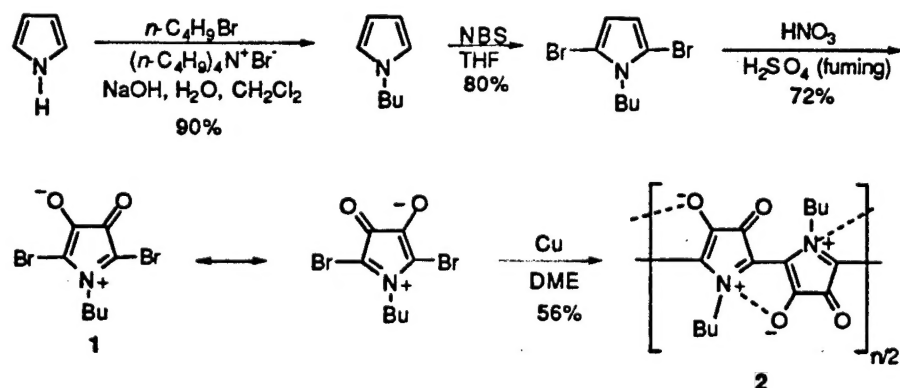
Thorsten W. Brockmann and James M. Tour\*

Department of Chemistry and Biochemistry  
University of South Carolina  
Columbia, South Carolina 29208

In an effort to maximize the extended  $\pi$ -conjugation in polymers and to study their corresponding electronic and optical properties, several have undertaken the synthesis of new conjugated organic polymers that have a planar or near-planar conformation between the consecutive repeat units.<sup>1,2</sup> Described here is the synthesis of a unique zwitterionic pyrrole-derived polymer that can reversibly convert to a linear and planar conjugated polymer with a solution band gap of approximately 1.1 eV. The material possesses a reversible and enormous pH-dependent or solvent dependent absorption spectral range from the UV to the near-IR spectral region. Soluble polymeric materials that can respond dramatically and reversibly to external stimuli could have importance in the development of organic-based optical and electronic sensors,<sup>2</sup> while polymers with absorbances in the near-IR can serve as dyes for optical data discs.<sup>3</sup>

The synthesis of the new pyrrole-derived zwitterionic polymer is described in Scheme 1.

Scheme 1



Accession For		
NTIS	CRA&I	<input checked="" type="checkbox"/>
DTIC	TAB	<input type="checkbox"/>
Unannounced		<input type="checkbox"/>
Justification _____		
By _____		
Distribution / _____		
Availability Codes		
Dist	Avail and/or Special	
A-1		

Pyrrole was N-alkylated under standard phase transfer conditions.<sup>4</sup> Bromination<sup>5</sup> and vigorous oxidation yielded the zwitterionic monomer **1**, a carbonyl-stabilized azomethine ylide, in an overall 52% yield for the three steps. The FTIR (KBr, 1718  $\text{cm}^{-1}$ , with no hydroxyl absorbance), mass spectrum (calc'd for  $\text{C}_8\text{H}_9\text{Br}_2\text{NO}_2$ : 311; found: 311), elemental analysis (calc'd: C, 30.89; H, 2.92; Br, 51.39; N, 4.50; found: C, 30.90; H, 2.92; Br, 51.25; N, 4.48), UV spectrum ( $\text{CH}_2\text{Cl}_2$ ,  $\lambda = 248, 322$ ; NMP,  $\lambda = 281, 320$  (sh); there was little change in the UV spectra in the presence of aqueous NaOH or aqueous HCl),  $^1\text{H}$  NMR [(300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.59 (t,  $J = 7.3$  Hz, 2 H), 1.57 (p,  $J = 7.1$  Hz, 2 H), 1.30 (sext,  $J = 7.3$  Hz, 2 H), 0.91 (t,  $J = 7.3$  Hz, 3 H)] and  $^{13}\text{C}$  NMR [(75 MHz,  $\text{CDCl}_3$ )  $\delta$  163.85, 129.24, 39.48, 30.39, 19.82, 13.52] were all consistent with the proposed structure. Note that two resonance forms exist for **1**, therefore there are only six peaks in the  $^{13}\text{C}$  NMR spectrum.

We then sought to polymerize **1** using a variety of coupling methods.<sup>6</sup>  $(\text{COD})_2\text{Ni}(0)$ ,<sup>7</sup> copper(II) triflate,<sup>8</sup> and Rieke copper<sup>9</sup> failed to afford any polymeric product. Classical Ullman<sup>10</sup> coupling using copper-bronze (Aldrich) also failed when utilizing the common solvents (DMF, quinoline, tetramethylurea, or pyridine), however, in DME, copper-bronze-promoted polymerization (200°C, screw cap tube) of **1** afforded the desired polymer **2** (Scheme 1) in 56% yield after fractional precipitation ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{OH}$ ). The precipitation dramatically sharpened the polydispersity (PD) to 1.15-1.25 with  $M_n = 3\ 130$  (SEC, PS standards).<sup>11</sup> Spectral analysis again confirmed the proposed structure.

The optical spectra for **2** are most interesting. Polypyrrole has an absorption maximum of 420 nm (solid) but it is intractable. N-alkylated polypyrroles can be soluble, however, the increased steric repulsions between the consecutive aryl units causes a hypsochromic shift to approximately 380 nm.<sup>6</sup> Remarkably, the absorption maximum of **2** exhibits a strong bathochromically shifted absorbance that may be due to ionic interactions that force a diminution in the inter-unit twist angle as depicted in Scheme 1.<sup>2</sup> Solvatochromic effects are consistent with this proposal in that the following trend of  $S_0$ - $S_1$  ( $\pi\pi^*$ )

absorption maxima are present for **2**: CCl<sub>4</sub>, 520 nm; THF, 512 nm (Figure 1); EtOH/THF (1:1), 503 nm; acetone, 482

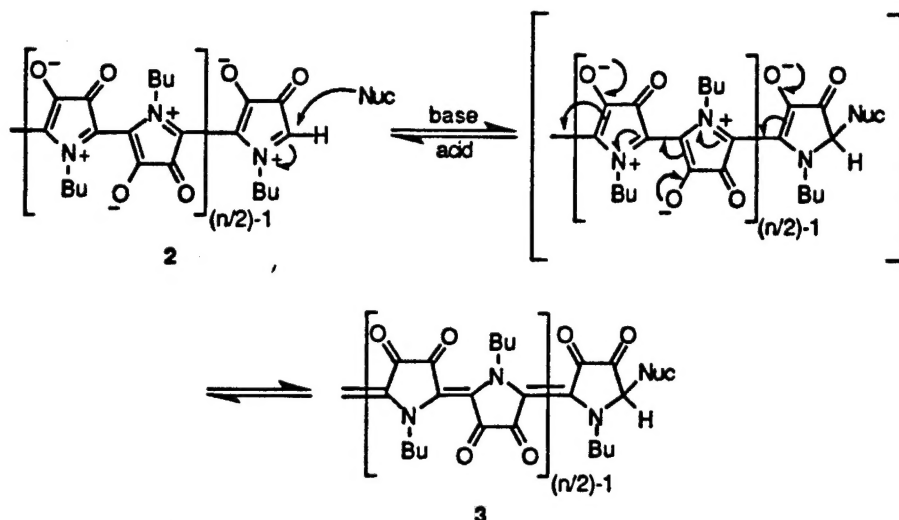
**Figure 1.** (a) Spectrum of **2** in THF (-----). (b) Dissolution of **2** in THF/aqueous NaOH to form **3** (----).

nm. Thus when the charges can be solvent stabilized, inter-unit stabilization/planarization is retarded and the absorption shifts hypsochromically. Likewise, stabilization of the polar ground state increases the energy gap of the  $\pi$ - $\pi^*$  transition which may exhibit charge transfer character.<sup>3,12</sup> Remarkably, when aqueous NaOH (0.05 M) was added dropwise to **2** in THF, the initial red-colored solution ( $\lambda_{\text{max}} = 512$  nm) became pale-orange and then finally brown ( $\lambda_{\text{max}} = 881$  nm) as more base was added (Figure 1). This pH-dependent shift in the absorption spectrum was reversible but polymer decomposition was detected after a few hours in the hydroxide-containing medium. Equally impressive solution effects occurred upon the dissolution of **2** in strongly Lewis basic solvents<sup>12</sup> such as HMPA ( $\lambda_{\text{max}} = 901$  nm) or NMP ( $\lambda_{\text{max}} = 746$  nm) (**2** was insoluble in DMSO) (Figure 2).<sup>13</sup> No polymer decomposition was

**Figure 2.** Dissolution of **2** in (a) HMPA (——) and (b) NMP (----).

detected in these Lewis basic solvents. Upon the addition of aqueous HCl, the HMPA and NMP solutions once again became red with no absorption bands present above 600 nm. The <sup>13</sup>C NMR spectrum of **2** in HMPA (with 10% CDCl<sub>3</sub> added for the lock) showed the butyl signals as well as a broad resonance from 176-163 ppm. In accord with the dramatic and reversible optical absorbance shifts, Brønsted or Lewis bases might be promoting a cascade of  $\pi$ -electron migrations in **2** to afford the planar conjugated polymer **3** (Scheme 2).

Scheme 2



Another interesting feature of **2** is that it could be partially reduced with  $H_2$  (1 atm) over Pd/C (24 h,  $23^\circ C$ ) to afford a system that is very similar to the starting polymer by FTIR, and SEC analysis, while the  $^1H$  NMR and  $^{13}C$  NMR showed peak broadening; therefore, some of the units were hydrogenated. Although the reduced polymer can not attain the degree of extended conjugation of **3** (as determined by the optical absorbances), its response range to different solvents can be from the UV region with weak tailing into visible, to the near-IR (DMSO,  $\lambda = 886$  nm) (Figure 3). Thus the reduced polymer is soluble in DMSO and it responds most dramatically to solvent changes.

**Figure 3.** Spectrum of the reduction product of **2**. (a) In THF (----) and (b) in DMSO (—).

**Acknowledgments.** Support came from the Office of Naval Research, the National Science Foundation (EHR-91-08772, DMR-9158315), and industrial contributors to the NSF Presidential Young Investigator Award Program (1991-96): Molecular Design Ltd., Hercules, IBM, Ethyl, Shell, Eli Lilly, Polaroid, Farchan, and Exxon Corporations.

### References and Notes

- (1) (a) Schlüter, A.-D. *Adv. Mater.* **1991**, *3*, 282. (b) Yu, L.; Chen, M. Dalton, L. R. *Chem. Mater.* **1990**, *2*, 649. (c) Scherf, U.; Müllen, K. *Synthesis* **1992**, 23. (d) Tour, J. M.; Lamba, J. J. S. *J. Am. Chem. Soc.* **1993**, *115*, 4935. (e) *Handbook of Conducting Polymers*; Skotheim, T. J., Ed.; Dekker: New York, 1986.
- (2) For some recent examples of reversible conjugated polymer backbone control, see: (a) Marsella, M. J.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 12214. (b) McCullough, R. D.; Williams, S. P.; Jayaraman, M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*(1), 190.
- (3) Zollinger, H. *Color Chemistry*; Chap. 14, VCH: New York, 1991.
- (4) Wang, N.; Teo, K.; Anderson, H. J. *Can. J. Chem.* **1977**, *55*, 4112.
- (5) Khoury, Y.; Kovacic, P.; Gilow, H. M. *J. Polym. Sci., Polym. Lett.* **1981**, *19*, 395.
- (6) For some background work on polypyrroles, see: (a) Street, G. B. in ref. 1e. (b) Bureau, J. M.; Gazard, M.; Champagne, M.; Dubois, J. C.; Tourillon, G.; Garnier, F. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 235.
- (7) Semmelhack, M. F.; Helquist, P. M.; Jones, L. D. *J. Am. Chem. Soc.* **1971**, *93*, 5908.
- (8) Cohen, T.; Cristea, I. *J. Org. Chem.* **1975**, *40*, 3649.
- (9) Matsumoto, H.; Inaba, I.; Rieke, R. D. *J. Org. Chem.* **1983**, *48*, 840.
- (10) (a) Bacon, G. R.; Stewart, O. J. *J. Chem. Soc. C* **1965**, 4653. (b) Groenendaal, L.; Peerlings, H. W. I.; van Dongen, J. L. J.; Havinga, E. E.; Vekemans, J. A. J. M.; Meijer, E. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*(1), 194.
- (11) Significant errors in  $M_n$  and  $M_w$  may result when comparing rigid rod polymers to the flexible coils of polystyrene (PS) standards by SEC. Therefore, the values recorded here are given simply as a reference.
- (12) (a) Kamlet, M. J.; Abboud, J.-L., M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877. (b) Effenberger, F.; Würthner, F. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 719. (c) Reichardt, C. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 98.
- (13) For some other low band gap conjugated polymers, see: (a) Wudl, F.; Kobayashi, M.; Heeger, A. J. *J. Org. Chem.* **1984**, *49*, 3382. (b) Pomerantz, M.; Chaloner-Gill, B.; Harding, L. O.; Tseng, J. J.; Pomerantz, W. J. *J. Chem. Soc., Chem. Commun.* **1992**, 1672. (c) Havinga, E. E.; ten Hoeve, W.; Wynberg, H. *Polym. Bull.* **1992**, *29*, 119. (d) Sandman, D. J. *Trends in Polym. Sci.* **1994**, *2*, 44.

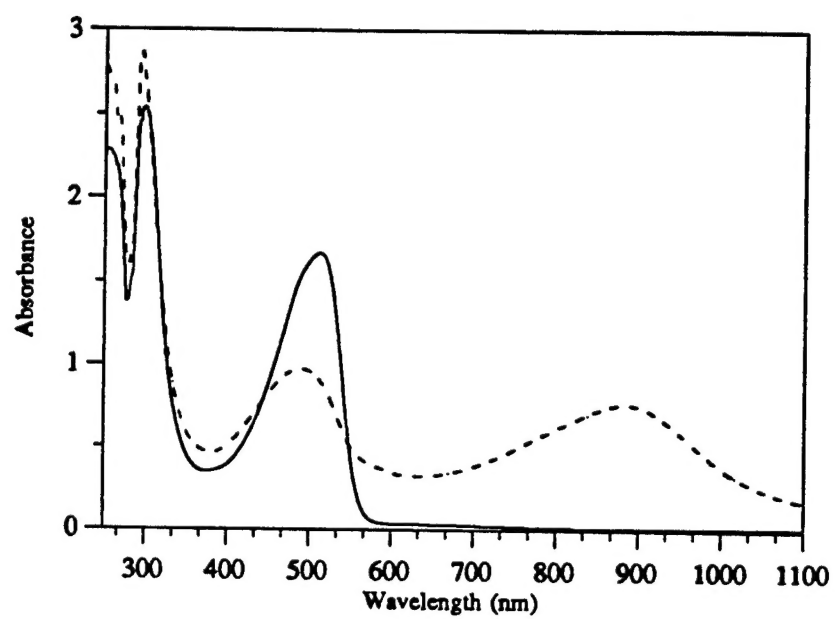


Fig 1



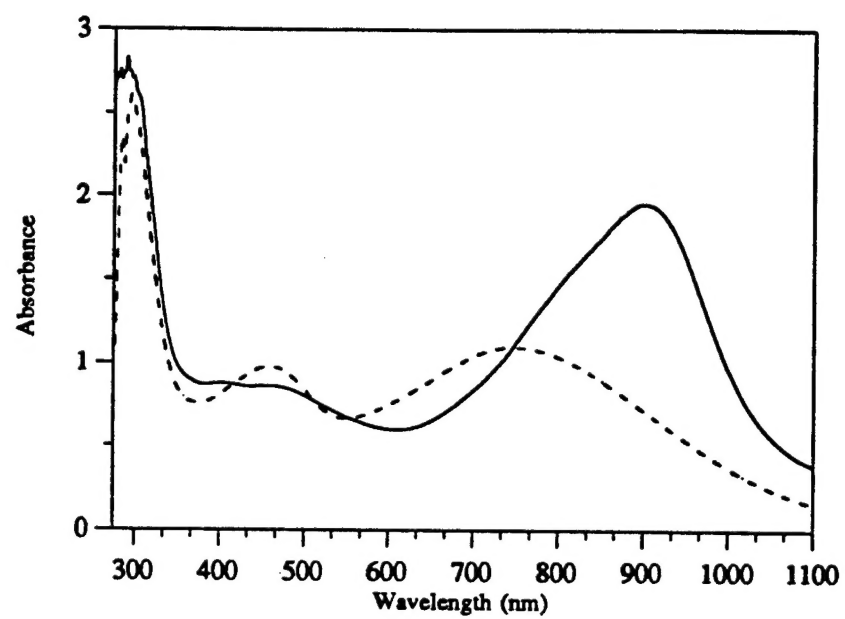


Fig 2

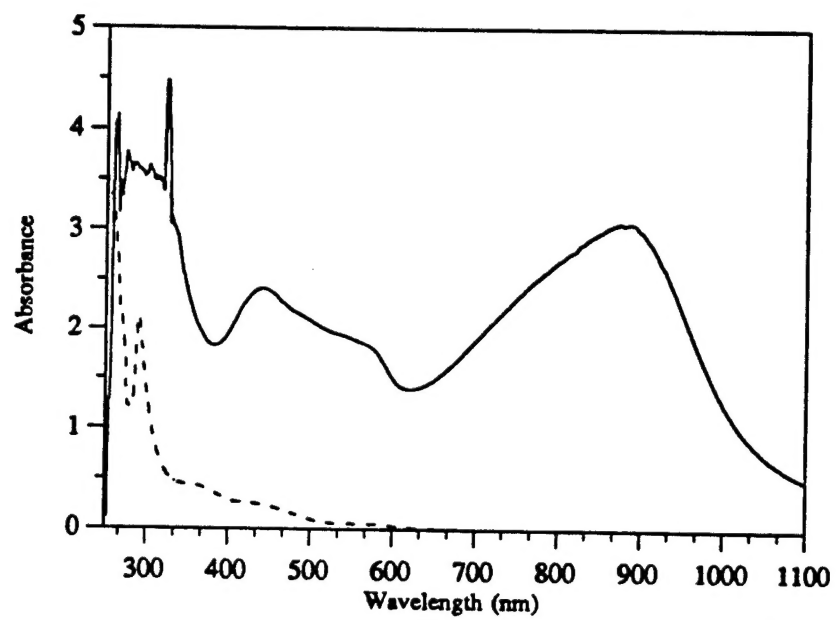


Fig 3